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BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

MAILED

MAR 1 3 2006

GROUP 1700

Application Number: 08/894,351
Filing Date: October 27, 1997
Appellant(s): REDECKER ET AL.

For Appellant

EXAMINER'S ANSWER

MAILED

MAR 1 6 2006

GROUP 1700

This is in response to the appeal brief filed 12/29/2005 appealing from the Office action mailed 9/8/2004.

(1) Real Party in Interest

A statement identifying by name the real party in interest is contained in the brief.

The examiner is not aware of any related appeals, interferences, or judicial proceedings which will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

(3) Status of Claims

The statement of the status of claims contained in the brief is correct.

(4) Status of Amendments After Final

The appellant's statement of the status of amendments after final rejection contained in the brief is correct.

(5) Summary of Claimed Subject Matter

The summary of claimed subject matter contained in the brief is correct.

(6) Grounds of Rejection to be Reviewed on Appeal

The appellant's statement of the grounds of rejection to be reviewed on appeal is correct.

WITHDRAWN REJECTIONS

The following grounds of rejection are not presented for review on appeal because they have been withdrawn by the examiner. The double patenting rejections have been withdrawn.

(7) Claims Appendix

The copy of the appealed claims contained in the Appendix to the brief is correct.

(8) Evidence Relied Upon

5,472,647	Blau et al	12-1995
5,500,059	Lund et al	3-1996
5,472,534	Wardle et al	12-1995
5,516,377	Highsmith et al	5-1996
0607446	Yoshida	7-1994
0519485	Redecker et al-full translation attached	12-1992

(9) Grounds of Rejection

The following ground(s) of rejection are applicable to the appealed claims:

Claims 1-4, 9-10, 27 and 31 are rejected under 35 U.S.C. 103(a) as being unpatentable over Blau et al., in view of Lund et al. '059, Wardle et al., Highsmith et al., Yoshida et al. '446 and Redecker et al. '485.

Blau et al. teach the basic invention which includes tetrazole fuel, with various oxidizers, including metal peroxides, perchlorates, nitrates, and mixtures thereof. Note the Abstract, col. 2, lines 30-32, col. 6, lines 1-21 and claim 26, part (a) with mixtures of oxidizers. Further detail is found at col. 5, lines 22-55 for fuels, and additives at col. 6, lines 31-57. Substitution of specific notoriously well

known ingredients, amounts or specific mixtures thereof would have been obvious to one of ordinary skill in the art. Note Lund et al. '059 col. 5, lines 1-25, e.g., as well as "Table 3" with a plurality of oxidizers, and claim 1 which claims mixtures of oxidizers. Wardle et al. teach zinc peroxide at col. 3, lines 20 and 22. Highsmith et al. generally suggests mixtures and the examples teach a plurality of oxidizers, e.g. Yoshida et al. '446, is further relevant, showing three oxidizers in "Table 1", "Example 15", e.g. Redecker et al. '485, shows examples with 5-AT and a plurality of oxidizers, including zinc peroxide and a plurality of other added conventional oxidizers.

It is well settled that optimizing a result effective variable is well within the expected ability of a person or ordinary skill in the art. In re Boesch, 617 F. 2d272, 205 USPQ 215 (CCPA 1980), In re Aller, 220 F. 2d 454, 105 USPQ 233 (CCPA 1955). Further, where the ingredients are well known and combined for their known properties, the combination is obvious, absent unexpected results, In re Crocket, 126 USPQ 186, In re Pinten, 173 USPQ 801, In re Sussman, 43 CD 518, and In re Susi, 169 USPQ 423. At best, this seems mere optimization of parameters by mixing known ingredients.

(10) Response to Argument

Applicant's arguments have been fully considered but they are not persuasive. The Blau and Lund references clearly disclose the use of multiple oxidizers in combination with the fuel as claimed. The Wardle reference is significant since it discloses the known use of zinc peroxide in a similar application. It is obvious to substitute one known oxidizer for another. The

Highsmith and Yoshida references generally show the use of multiple oxidizers with further emphasis on Yoshida in Table 1 which shows three oxidizers being used. Redecker is also important for showing that it is known to use zinc peroxide in combination with other oxidizers.

Applicant argues unexpected results and these arguments are also not persuasive. The claimed combination is obvious and one must consider the extent of unexpected results which is not substantial, if present at all, in the instant application. The evidence relied upon should establish "that the differences in results are in fact unexpected and unobvious and of both statistical and practical significance." Ex parte Gelles, 22 USPQ2d 1318, 1319 (Bd. Pat. App. & Inter. 1992). Also, where the unexpected properties of a claimed invention are not shown to have a significance equal to or greater than the expected properties, the evidence of unexpected properties may not be sufficient to rebut the evidence of obviousness. In re Nolan, 553 F.2d 1261, 1267, 193 USPQ 641, 645 (CCPA 1977).

(11) Related Proceeding(s) Appendix

No decision rendered by a court or the Board is identified by the examiner in the Related Appeals and Interferences section of this examiner's answer.

For the above reasons, it is believed that the rejections should be sustained.

Respectfully submitted,

Aileen Felton

Conferees:

Jerry Lorengo

Patrick Ryan

PTO 06-2496

European Patent 0 519 485 A1

PROPELLANT FOR GAS GENERATORS

Klaus Redecker and Waldemar Weuter

UNITED STATES PATENT AND TRADEMARK OFFICE
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PROPELLANT FOR GAS GENERATORS

[Treibmittel für Gasgeneratoren]

Inventors:	Dr. Klaus Redecker and Dr. Waldemar Weuter
Applicant:	Dynamit Nobel AG

Gas generators are finding increasing interest for life-saving, for example, in vehicles. The most widely employed mixture worldwide for generation of gas contains sodium azide. Sodium azide, however, is toxic, which requires special measures in the production of raw material, gas charge mixing, its processing, quality control and disposal. This is especially true during scrapping of vehicles.

There has been no lack of attempts to use substances other than sodium azide. DE-A-21 42 578 describes a compressed propellant charge for rapid inflation of a hollow element by converting tetrazolyltetrazenes with oxygen carriers. DE-A-18 06 550 proposes a compressed gas-generating propellant charge that produces cool gases based on ammonium nitrate, activated carbon and a compound that decomposes or sublimes endothermically.

However, this system produces a large amount of water vapor, which is a shortcoming, because water leads to a sharp temperature increase because of its high heat of condensation.

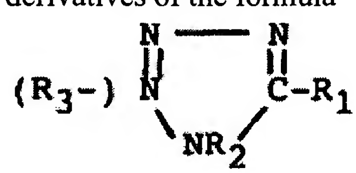
DE-A-12 22 418 describes mixtures that develop compressed gas based on inorganic perchlorate oxidizers, polymer fuel binders and a coolant. Preparations with high percentages of chlorate or perchlorate, however, lead to chlorine fractions in the reaction gases. EP-A-372 733 also describes an unsatisfactory mixture, since the propellant charge of the proposed air bag contains about 40% ammonium perchlorate. Even nitrocellulose and nitroglycerine masses can be found in the literature. Such proposals are not usable for applications in life-saving systems. Nitrocellulose and nitroglycerine mixtures or other carbon-rich, high-energy compounds fail because of formation of carbon monoxide.

The propellant charges of DE-A-12 50 318, which contain aminotetrazole, potassium dichromate, calcium resinate and metallic silicon, also do not meet present safety requirements. The same applies to DE-C-20 04 620, whose compressed gas-generating charge contains azotetrazole and/or ditetrazole and chlorate or perchlorates. The propellant charges of US-A-3 734 789, which contain 5-aminotetrazole nitrate and polyisoprene binders do burn up quickly, but generate carbon monoxide in health-hazardous concentration because of the carbon-rich binder fraction.

The underlying task of the invention is to furnish gas charges whose production and processing and handling are safe and whose conversion products are nontoxic.

This task is solved by a propellant for gas generators, which contains as nitrogen-containing compound

a) one or more tetrazole derivatives of the formula



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in which R_1 and R_2 or R_3 can be the same or different, but either R_2 or R_3 is present and has the meaning: hydrogen, hydroxy, amino, carboxyl, an alkyl group with 1 to 7 carbon atoms, an alkenyl group with 2 to 7 carbon atoms, an alkylamino group with 1 to 10 carbon atoms, an aryl group, optionally substituted with one or more substituents that can be the same or different, chosen from the amino group, nitro group, alkyl groups with 1 to 4 carbon atoms or an arylamino group in which the aryl group can optionally be substituted, or their sodium, potassium and guanidinium salts

or which contain as nitrogen-containing compounds

b) one or more compounds from the groups

A) cyanic acid derivatives and their salts,

B) triazine and triazine derivatives,

C) urea, its salts, derivatives and their salts,

in which the compounds mentioned under a) and b) can also be present as mixtures, and an oxidizing agent from the group of peroxides or from the group of peroxides together with oxidation agents from the group of nitrates.

The nitrogen-containing compounds to be used according to the invention are those that form mostly CO_2, N_2 and H_2O in a mixture with oxidizers during their thermal/chemical conversion, but no gases like CO or NO_x in health-hazardous concentrations. It is of particular significance that the addition of binders is not absolutely necessary.

R_1 preferably denotes hydrogen, amino, hydroxy, carboxyl, a methyl, ethyl, propyl or isopropyl, butyl, isobutyl or tert-butyl, n-pentyl, n-hexyl or n-heptyl group, a methylamino, ethylamino, dimethylamino, n-heptylamino, n-octylamino or n-decylamino group, a phenylamino group, a phenyl, nitrophenyl or aminophenyl group.

R_2 or R_3 preferably denotes hydrogen, a methyl or ethyl group, a phenyl, nitrophenyl or aminophenyl group.

The following tetrazole derivatives are particularly preferred: 5-aminotetrazole, sodium, potassium or calcium-5-aminotetrazolate, 1-(4-aminophenyl)tetrazole, 1-(4-nitrophenyl)tetrazole, 1-methyl-5-dimethylaminotetrazole, 1-methyl-5-methylaminotetrazole, 1-methyltetrazole, 1-phenyl-5-aminotetrazole, 1-phenyl-5-hydroxytetrazole, 1-phenyltetrazole, 2-ethyl-5-amino-tetrazole, 2-methyl-5-aminotetrazole, 2-methyl-5-carboxyltetrazole, 2-methyl-5-methylamino-tetrazole, 2-methyltetrazole, 2-phenyltetrazole, 5-(p-tolyl)tetrazole, 5-diallylaminotetrazole, 5-dimethylaminotetrazole, 5-ethylaminotetrazole, 5-hydroxytetrazole, 5-methyltetrazole, 5-methylaminotetrazole, 5-methylaminotetrazole [sic], 5-n-decylaminotetrazole, 5-n-heptyl-aminotetrazole, 5-n-octylaminotetrazole, 5-phenyltetrazole, 5-phenylaminotetrazole or bis(aminoguanidine)azotetrazole.

Sodium cyanate, cyanuric acid, 1-cyanoguanidine and/or disodium cyanamide are preferred as cyanic acid derivatives, 1,35-triazine, cyanuric acid esters and/or cyanuric acid amide (melamine) as triazine derivatives, and biuret, guanidine, nitroguanidine, guanide nitrate, aminoguanidine, aminoguanidine nitrate, triaminoguanidine nitrate, aminoguanidine hydrogen carbonate, azodicarboxylic acid diamide, dicyandiamidine nitrate, dicyandiamidine sulfate, tetrazene and/or semicarbazide nitrate can be used as urea derivatives.

In addition to health safety, the mixtures according to the invention possess high thermal and climatic stability, which is a prerequisite for perfect effect even after longer storage.

Nitrates of ammonium, sodium, potassium, magnesium, calcium or iron can be used as oxidizers, preferably sodium nitrate or peroxides of zinc, calcium, strontium or magnesium.

The peroxides are then used with an oxygen value as can be obtained from stable compounds. For zinc peroxide this lies at about 11 to 14 wt%. The corresponding molar ratio of nitrogen-containing compounds of peroxide then lies in the range from 1:2 to 5.5. Calcium peroxide can have an active oxygen value of, say, 18.62 wt% and particle sizes of 15.5 μm and is advantageously used in a molar ratio of nitrogen compound to peroxide 1:3. Generally the aforementioned peroxides can be used in a molar ratio of 1:1 to 20.

Calcium and/or zinc peroxide is preferably used. Mixtures of peroxides with each other or mixtures with other oxidizers can also be used. Other oxidizers include the aforementioned nitrates of ammonium, sodium, potassium, magnesium, calcium or iron, preferably sodium nitrate.

When magnesium and especially calcium or strontium peroxide is used, reactions with the other components of the mixture can occur because of the hydrolysis products with an alkaline effect. Coating of the peroxides with inorganic or organic materials according to known methods is expedient here. Such coating also offers the advantage of better handling capability, since propellants treated in this way no longer produce dust.

The mixtures to be used according to the invention from tetrazole or its derivatives with compounds from groups A), B) and/or C) permit finely graded gradation of the propellants with reference to their reaction rate and the developing vapors and gases. Gradation is essential in order to be able to use the propellants according to the invention with as much versatility as possible. Depending on the design of the generator housing of, for example, an airbag or belt tightener, the propellant charges according to the invention must be purposefully mixed. Only then is it possible to achieve an optimal effect. The efficiency of the propellant charges according to the invention is influenced not only by the composition, but also by ignition and also by damming caused by the design and by the outflow behavior of developing vapors and gases. Evaluation of the efficiency can be made, for example, by determining the gas pressure rise gradient of the corresponding mixture in the external environment stipulated by the corresponding design and the chosen type of ignition. The developing gas concentration, especially that of health-hazardous gases, must not surpass certain maximum values. These values are obtained from the MAC values (or from the TLV values in the US). Technical requirements that the corresponding propellant charges must satisfy are established from these values together with the permitted exposure times. In establishing these requirements, different passenger compartments are also included. To satisfy these requirements deliberate mixing of the corresponding propellant charge is required.

The values shown in table were determined by igniting 4 g of the corresponding propellant charge in a pressure bomb of 25 mL volume with an incandescent wire in a cup in a

loose bed. After ignition a pressure/time curve was recorded. The resulting values were evaluated as follows:

(1) Maximum pressure (bar): with the same weighed amount difference are attributed directly to the formed gas volumes. These are determined by the gas yield and heat effect of the reaction.

(2) Gas pressure increase for the range from 40-60% of maximum pressure: in this range the curve is no longer distorted by the burn-up or cooling behavior of the vapors for the internal bomb surface. The stated time in milliseconds (ms) gives the pressure increase and denotes different conversion rates. Such values are also obtained in the corresponding applications; for example, in the different gas generator housings that vary in design. They permit precise adjustment of the propellant charges according to the invention with respect to performance requirements. By stating the pressure increase times in the range from 40 to 60% of the maximum pressure, the conversion rate of the propellant charges according to the invention is sufficiently characterized. The times for conversion up to occurrence of maximum pressure are used for additional information.

Keeping the gas temperature low can be deliberately achieved by adding diammonium oxalate, oxalic acid diamide, dicyandiamide or carbonates or bicarbonates. If thermal stability does not matter and smoke formation is to be avoided during addition of inorganic carbonates or bicarbonates, aminoguanidine bicarbonate can be used as the organic bicarbonate. Additional additives can be oxalic acid or urea, which are generally added in an amount of up to 5 wt% write reference to the mixture.

Metal powders of iron, magnesium, zirconium or titanium can be added as reducing agents, which in contrast to the nonmetal boron, have no significant effect on burn-up rate but do have an effect on the heat effect of the conversion and the reaction products. The percentage of reducing agent can be up to 5 wt%.

Compounds that have an effect on the decomposition of peroxides, like metals or their oxides; for example, manganese dioxide are suitable as catalysts for such a heterogeneous mixture. Additives of vanadium pentoxide or cerium dioxide lead to an increase in conversion rate. When 5 wt% molybdenum(VI) oxide is added, it is only slightly altered, as in the presence of cerium(III) nitrate hexahydrate. These additives are effective in amounts of up to a few wt%. Additional catalysts are metal complexes, among which ferrocene can be mentioned as an example, addition of which to about 3 wt% significantly increases the reaction rate.

Preparation of the gas charges described according to the invention occurs by mixing the components according to known methods, optionally with production of a safe premix to which additional components are added. The mixture can be used in already powdered form. Demixing by different density of the components can be countered by granulation of the mixture.

In by far the most frequent applications, the mixture is formed by pressing or similar measures. Press auxiliaries can be added to the mixture for simplification of this method. Graphite, molybdenum disulfide, teflon, talc, zinc stearate or boron nitride are considered as such. These agents already act in limited amounts and influence the properties and burn-up behavior not at all or only slightly.

In many cases it can be advantageous to influence the burn-up characteristics of the molding by porosity generation. Once such method consists of adding such additives as salts before actual forming of the mixture, which can be removed again by extraction with water or solvents after shaping. Another method consists of adding substances that are not very heat resistant, that decompose when the molding is heated. The surface of the mixture can also be increased by adding hollow microspheres made of glass or plastics to the mixture before pressing. The density of the molding achieved by this can deviate up to 20% from the untreated molding, but this value is only a rough guideline and does not represent a restriction. This treatment leads to extreme acceleration of the burn-up process.

Another treatment of the molding consists of surface coating. In this case, in addition to influencing the burn-up characteristics, protection against environmental effects is achieved. Such measures can also be appropriate for increasing the strength of the molded article. In extreme cases the use of appropriate fibers for stabilization could additionally be prescribed here. A side effect of coating is a reduction in abrasion during transport stress on the parts.

The moldings so treated could be introduced loosely or aligned in the corresponding pressure-tight containers. They are ignited according to usual methods with ignition charges or thermal charging in which the forming gases lead to filling of the life-saving system in fractions of a second, optionally after passing through an appropriate filter.

The propellants according to the invention are especially suitable for so-called airbags, impact bags that are used in vehicles or aircraft to protect occupants. During impact of a vehicle the airbag must be filled within the shortest time with gas mixtures of about 50 to 300 L, depending on the system and vehicle size. The propellants according to the invention are also suitable for use in seat-belt tighteners.

Life-saving systems that contain the propellants according to the invention are also the object of the present invention.

Example 1

167 g 5-aminotetrazole (5-ATZ) (prepared from aminoguanidine sulfate, sodium nitrite and nitric acid) is recrystallized from about 600 mL water during continuous agitation, dried after filtration at 110°C, ground and separated with a 250 μm sieve from the coarse fractions (5-ATZ specification: mp/decomposition: >203°C, average particle size 80 μm and H_2O percentage

<0.05%). ZnO_2 is prepared from $ZnSO_4 \times 7H_2O$ and hydrogen peroxide in ammonia water, washed with dilute acetic acid and water and dried at 60°C (specification of ZnO_2: 13.47 wt% active oxygen, average particle size 10.3 μm).

5-ATZ and ZnO_2 as components for nontoxic gas charges are homogenized together in a weight ratio of 1 to 7 (this corresponds to a molar ratio of about 1:5) in plastic containers in a tumble mixer from 1 to 2 hours. 3.0 g of the sample are introduced as loose product in a 25 mL stainless steel pressure bomb and made to react with an electrically heatable Fe wire and a pressure-time trend recorded by means of a piezoelectric measurement device. A maximum gas pressure of about 200 bar develops after about 30 ms, which is mostly attributed to formation of CO_2, N_2, O_2 and H_2O. The reaction has strong exothermic characteristics of about 471 cal/g (about 1970 J/g). ZnO remains as reaction residue. The CO fraction corresponds to the requirement. The deflagration point lies at 219°C, friction sensitivity at 240 N, impact sensitivity at 20 J.

Examples 2 to 24

The use of 5-ATZ and ZnO_2 as components in nontoxic gas charges corresponds to Example 1 using additional additives. The following Examples 2 to 24 describe conversion of the mixtures produced in known fashion. The results are summarized in Tables 1 to 4.

Table 1

Example No.	Organic additives (mol)									Reaction rate (measured as in exam ple 1)
	2	3	4	5	6	7	8	9	10	
5-Aminotetrazole	1	1	1	1	1	1	1	1	1	
Zinc peroxide	3	3	3	3	3	3	3	3	3	
Ammonium nitrate	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	rose relative to 1
Aminoguanidine nitrate										rose relative to 2
Urea		1								dropped relative to 2
Oxalic acid dihydrate			1							dropped relative to 2
Oxalic acid diamide				1						dropped relative to 2
Diammonium oxalate monohydrate					1					dropped relative to 2
Semicarbazide nitrate						1				rose relative to 2
Aminoguranidine hydrogen carbonate							1			dropped relative to 2
Ferrocene								1	1×10^{-1}	rose relative to 2

Table 2

Example No.	Inorganic additives (mol)						
	11	12	13	14	15	16	
5-Aminotetrazole	1	1	1	1	1	1	
Zinc peroxide	3	3	3	3	3	3	
Ammonium nitrate	1.5	2.5	2.5	2.5	2.5	2.5	
Iron nitrate nonahydrate	1.6×10^{-2}						dropped relative to 2
Zinc carbonate		2×10^{-3}					dropped relative to 2
Molybdenum(VI) oxide			3×10^{-3}				comparable to 2
Sodium nitrate				1			dropped relative to 2
Strontium nitrate					1		dropped relative to 2
Calcium peroxide						1.5	comparable to 2

Table 3

Example No.	Catalyst additives (mol)								
	17	18	19	20	21	22	23	24	
5-Aminotetrazole	1	1	1	1	1	1	1	1	
Zinc peroxide	3	3	3	3	3	3	3	3	
Ammonium nitrate	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	
Vanadium(V) oxide	4×10^{-5}								rose relative to 2
Cerium(IV) oxide		5×10^{-5}							rose relative to 2
Cerium(IV) nitrate hexahydrate			4×10^{-5}						comparable to 2
Manganese(IV) oxide				9×10^{-5}					comparable to 2
Titanium					2×10^{-3}				comparable to 2
Iron						1×10^{-3}			comparable to 2
Magnesium							3×10^{-3}		comparable to 2
Boron								7×10^{-3}	rose relative to 2

Example 25

The gas mixtures described in Examples 1 to 24 can also be used in compressed form. A mixture of 10 g 5-ATZ (H_2O fraction <0.1%, melting point (decomposes) >203°C, particle size 200-250 μm), 43.9 g ZnO_2 (12.85 wt% active oxygen, particle size about 14 μm) and 23.5 g NH_4NO_3 (melting point 167-169°C, particle size 315-250 μm), molar ratio 1:3:2.5 are mixed according to Example 1 and pressed to tablets (diameter = 6 mm, height = 2.77 mm, density = 2.18 g/cm^3, radial compression force 155.5±28.4 N) with 4 t compression pressure. The burn-up behavior of the moldings, tested according to Example 1 is slower than that of the bulk charge and requires 0.1 g B/KNO_3 or Ti/ZnO_2 as ignition mixture. The conversion rate rises with a reduction in compression pressure and drops with size of the pressed product. The residue from the conversions is retained largely in the form of moldings.

Examples 26 to 32

As described in Example 1, additional mixtures were prepared from gas-generating components and oxygen suppliers like zinc peroxide with an active oxygen fraction of 13.07 wt% and an average particle size of 11.8 μm or in the case of sodium nitrate with average particle size <45 μm.

The following Table 4 contains additional data on the mixtures.

Table 4

Components	Mp (°C)	Molar ratio of mixture						
		26	27	28	29	30	31	32
5-Aminotetrazole	206-208	1						
Potassium-5-aminotetrazolate	269		1					
Bis(aminoguanidine)azotetrazole	224-226			1				
Nitroguanidine	252				1			
Guanidine nitrate	210-214					1		
Semicarbazide nitrate	115-119						1	
1-Cyanoguanidine	208-210							1
Zinc peroxide	200 (decomp)	2.48	2.48	10.64	1.42	1.42	0.71	4.25
Sodium nitrate	–	0.83	0.83	3.55	0.47	0.47	0.24	1.42

The components were homogenized in plastic containers for ½ hour with a tumble mixer, 1/2 hour with a vibrator and 1/2 hour again with a tumble mixer.

4 g of the mixture so homogenized were introduced as described in Example 1 to a stainless steel pressure bomb and brought to conversion after closure by ignition with incandescent wire. The following were measured:

– the forming pressure (bar) up to the maximum value

– the time (milliseconds, ms) up to the maximum pressure value

– the pressure increase gradient (dp/dt) between a pressure that reaches 40 to 60% of the maximum pressure. The rise time served as gauge.

The following Table 5 shows the values for the maximum pressure (bar) and the time in ms of the maximum pressure, which lie in the range as described in Example 1 for a gas charge from 5-aminotetrazole and zinc peroxide. The time between 40-60% of the maximum pressure was additionally determined.

Table 5

Example No.	Maximum pressure (bar)	Time (ms)	
		to maximum pressure	to 40-60% maximum pressure
26	359	30	1.2
27	217	123	13.1
28	352	29	1.5
29	473	39	1.3
30	549	14	0.5
31	917	7	0.2
32	148	220	20.1

By determining the parameters and adding additional components the requirements necessary for a corresponding gas charge can be set.

Another sample of the aforementioned mixtures was investigated for physical safety engineering properties. The results are described in Table 6.

Table 6

Example No.	Deflagration point (°C)*	Friction	Impact	Heat of explosion (J/g)
		sensitivity*		
		(N)	(J)	
26	180	>360	7.5	2451
27	207	>360	10	2293
28	197	>360	4	2411
29	215	>360	20	2964
30	364	>360	15	2777
31	210	>360	2	3128
32	194	>360	30	2101

* Determination occurred according to the method of the Federal Office for Material Testing (BAM) in Berlin.

Components are suitable for production of gas charges because of their miscibility, processability, compressibility for shaping and compatibility with one another and with additional additives, as well as their safety engineering characteristics.

Examples 33 to 44

As described in Examples 26 to 32, the mixtures of Examples 33 to 44 were produced from zinc peroxide (active oxygen fraction 12.8 wt%, average particle size 4.8 μm), aminotetrazole (average particle size ≤125 μm), sodium nitrate (particle size ≤45 μm) and the listed components with a particle size ≤125 μm.

The friction sensitivity measured according to the method of BAM was >360 N in all cases. The additionally listed components are described in the literature.

The following Tables 7 and 8 contain additional data on the mixtures.

Table 7

	Formulas	Wt%	Mol fractions
Example No. 33:	5-ATZ Zinc peroxide Sodium nitrate	29.8 23.4 46.8	1.4 0.75 2.2
Example No. 33:	5-ATZ Dicyandiamidine nitrate Zinc peroxide Sodium nitrate	19.5 15.2 21.5 43.8	1.0 0.4 0.75 2.24
Example No. 35:	5-ATZ Dicyandiamidine nitrate Zinc peroxide Sodium nitrate	18.1 12.8 19.8 49.3	1.0 0.2 0.75 2.73
Example No. 36:	5-ATZ 1-Cyanguanidine Zinc peroxide Sodium nitrate	19.5 7.7 21.4 51.4	1.0 0.4 0.75 2.64
Example No. 37:	5-ATZ Melamine Zinc peroxide Sodium nitrate	16.9 10.0 18.6 54.5	1.0 0.4 0.75 3.22
Example No. 38:	5-ATZ Azodicarboxylic acid diamide Zinc peroxide Sodium nitrate	20.2 11.0 22.2 46.6	1.0 0.4 0.75 2.31
Example No. 39:	5-ATZ Cyanuric acid Zinc peroxide Sodium nitrate	19.6 11.9 21.4 47.1	1.0 0.4 0.75 2.41
Example No. 40:	5-ATZ Urea Zinc peroxide Sodium nitrate	22.5 6.4 24.7 46.4	1.0 0.4 0.75 2.06
Example No. 41:	5-ATZ Biuret Zinc peroxide Sodium nitrate	20.2 9.8 22.2 47.8	1.0 0.4 0.75 2.37
Example No. 42:	5-ATZ Aminoguanidine nitrate Zinc peroxide Sodium nitrate	21.0 13.5 23.0 42.5	1.0 0.4 0.75 2.03
Example No. 43:	5-ATZ Sodium dicyanamide Zinc peroxide Sodium nitrate	20.5 8.6 22.5 48.4	1.0 0.4 0.75 2.37
Example No. 44:	5-ATZ Sodium cyanate Zinc peroxide Sodium nitrate	23.9 7.3 26.2 42.6	1.0 0.4 0.75 1.79

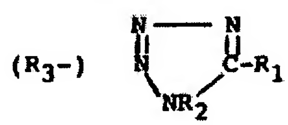
Table 8

Mixing components in mol fractions		Zinc peroxide	5-Aminotetrazole	Potassium nitrate	Pressure increase for the range 40-60% p_{max} (ms)	Maximum pressure (bar)	Heat of explosion (J/g)	Impact sensitivity (J)	Deflagration point (°C)	Example No.
		0.75	1.4	2.2	0.38	683	3258	5	>400	33
Dicyandiamidine nitrate	0.4	0.75	1.0	2.24	0.40	761	3142	6	>400	34
Dicyandiamidine sulfate	0.2	0.75	1.0	2.73	1.04	656	2883	7.5	395	35
1-Cyanguanidine	0.4	0.75	1.0	2.64	0.36	661	3038	10	367	36
Melamine	0.4	0.75	1.0	3.22	1.16	652	3187	10	>400	37
Azodicarboxylic acid diamide	0.4	0.75	1.0	2.31	0.36	706	3191	6	>400	38
Cyanuric acid	0.4	0.75	1.0	2.41	0.80	582	2732	7.5	>400	39
Urea	0.4	0.75	1.0	2.06	0.40	654	3053	10	>400	40
Biuret	0.4	0.75	1.0	2.37	0.56	663	2982	7.5	363	41
Aminoguanidine nitrate	0.4	0.75	1.0	2.03	0.30	693	3190	7.5	256	42
Sodium dicyanamide	0.4	0.75	1.0	2.37	0.36	486	3226	7.5	356	43
Sodium cyanate	0.4	0.75	1.0	1.79	0.34	458	3005	10	349	44

Claims

1. Propellants for gas generators for nitrogen-containing compounds characterized by the fact that they contain

a) one or more tetrazole derivatives of the formula



,

in which R_1 and R_2 or R_3 can be the same or different, but either R_2 or R_3 is present and has the meaning: hydrogen, hydroxy, amino, carboxyl, an alkyl group with 1 to 7 carbon atoms, an alkenyl group with 2 to 7 carbon atoms, an alkylamino group with 1 to 10 carbon atoms, an aryl group, optionally substituted with one or more substituents that can be the same or different, chosen from the amino group, the nitro group, alkyl groups with 1 to 4 carbon atoms or an arylamino group in which the aryl group can be optionally substituted, or their sodium, potassium and guanidinium salts

or that they contain

b) one or more compounds from the groups

A) cyanic acid derivatives and their salts,

B) triazine and triazine derivatives,

C) urea, its salts, derivatives and their salts,

in which the compounds mentioned under a) and b) can also be present as mixtures and an oxidizer from the group of peroxides or from the group of peroxides together with oxidizers from the group of nitrates.

2. Propellants according to Claim 1, characterized by the fact that R_1 or R_2 or R_3 can be the same or different but either R_2 or R_3 is present and denotes hydrogen, amino, methyl, phenyl, nitrophenyl or aminophenyl

or

R_1 denotes amino, hydroxy or carboxyl and R_2 or R_3 denote hydrogen, methyl or phenyl.

3. Propellants according to one of the Claims 1 or 2, characterized by the fact that 5-aminotetrazole, potassium-5-aminotetraolate and/or bis(aminoguanidine)azotetrazole are contained as tetrazole derivatives, sodium cyanate, cyanuric acid, 1-cyanoguanidine and/or disodium cyanamide are contained as cyanic acid derivatives, 1,3,5-triazine, cyanuric acid esters and/or cyanuric acid amide (melamine) are contained as triazine derivatives and/or biuret, guanidine, nitroguanidine, guanidine nitrate, aminoguanidine, aminoguanidine nitrate, aminoguanidine hydrogen carbonate, azodicarboxylic acid diamide, dicyandiamidine nitrate, dicyandiamidine sulfate, tetrazene and/or semicarbazide nitrate are contained as urea derivatives.

4. Propellants according to one of the Claims 1 to 3, characterized by the fact that nitrates of ammonium, sodium, potassium, magnesium, calcium or iron, preferably sodium nitrate and/or peroxides of zinc, calcium, strontium or magnesium, preferably zinc peroxide are contained as oxidizers.

5. Propellants according to one of the preceding claims, characterized by the fact that the molar ratio of nitrogen-containing compound to oxidizer lies in the range from 1:1 to 20.

6. Propellants according to one of the preceding claims, characterized by the fact that the molar ratio of nitrogen-containing compound to zinc peroxide lies in the range from 1:2 to 5.5, of nitrogen-containing compound to calcium peroxide in the range from 1:3.

7. Propellants according to one of the preceding claims, characterized by the fact that coolants, reducing agents and catalysts are contained as additional additives.

8. Propellants according to Claim 7, characterized by the fact that ferrocene is contained as catalyst.

9. Method for production of propellants for gas generators according to one of the preceding claims, characterized by the fact that the tetrazole derivative or derivatives and/or the compound or compounds from which A), B) and/or C) are mixed with the oxidizer or oxidizers and optionally with additional additives and the mixture homogenized.

10. Method according to Claim 9, characterized by the fact that the propellant, if necessary, is compressed using compression auxiliaries like graphite, molybdenum sulfide, telfon, talc, zinc stearate or boron nitride.

11. Method according to Claim 10, characterized by the fact that the moldings are coated.

12. Method according to Claim 10 or 11, characterized by the fact that a defined porosity of the molding is produced by controlling the burn-up rate.

13. Life-saving system containing a propellant according to one of Claims 1 to 8.

European
Patent Office

Application Number
EP 92 11 0353

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.^{5})
X	DE-A-2 063 586 (ASAHI KASEI KOGYO K.K.) * Claims; Example 7 *	1, 9, 13	C06D5/06 C06B43/00
X	CHEMICAL ABSTRACTS, Vol. 084, No. 18, May 3, 1976, Columbus, Ohio, US; Abstract No. 124138e, H. SHIMIZU ET AL. 'Gas forming compositions' Page 138; * Summary * & JP-A-75 118 979 (NIPPON OILS AND FATS CO., LTD)	1, 9, 10, 13	
A	DE-C-3 933 554 (BAYERN-CHEMIE GESELLSCHAFT FÜR FLUGCHEMISCHE ANTRIEBE MBH) * Claims *	9-11	TECHNICAL FIELDS SEARCHED (Int. Cl.^{5})
X	US-A-4 386 979 (C.H. JACKSON, JR.) * Column 2, Line 39 – Column 60; Claims * * Column 4, Line 48 – Column 61 * * Column 6, Line 8 – Column 16 *	1, 7, 9, 10, 13	C06D C06B
P, X	EP-A-0 482 852 (AUTOMOTIVE SYSTEMS LABORATORY INC.) * Claims; Example 5 *	1-4, 7, 9-11, 13	

The present search report has been drawn up for all claims.

Place of search	Date of completion of the search	Examiner
The Hague	October 5, 1992	SCHUT R.J.

CATEGORY OF CITED DOCUMENTS

X: Particularly relevant if taken alone.
Y: Particularly relevant if combined with another document of the same category.
A: Technological background.
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P: Intermediate document.

T: Theory or principle underlying the invention.
E: Earlier patent document, but published on, or after the filing date.
D: Document cited in the application.
L: Document cited for other reasons.

&: Member of the same patent family, corresponding document.